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**METHOD AND SYSTEM
FOR CANCELLATION OF EXTRANEEOUS SIGNALS
IN NUCLEAR QUADRUPOLE RESONANCE SPECTROSCOPY**

This invention relates generally to a bulk substance detection system employing nuclear quadrupole resonance (NQR) for detecting concealed explosives and drugs, and more particularly to a pulse sequence for use in NQR for cancellation of, among others, magneto-acoustic ringing, piezoelectric ringing, electronic circuit ringing (pulse ringdown), and baseline offset.

In the fight against terrorism, and for other purposes, there is a great need for a system that can quickly and reliably detect hidden explosives. Plastic explosives, for example those containing RDX and PETN, such as C-4 and Semtex, are highly stable, have clay-like malleability, and are deadly in relatively small quantities. Plastic explosives have an almost infinite variety of possible shapes and uses for

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terrorist bombing tactics. For example, a small piece of plastic explosive, a detonator, and a trip wire inside a large mailing envelope can cause a deadly explosion. Unfortunately, without close and potentially dangerous visual inspection, plastic explosives can be made virtually undetectable. For example, plastic explosives that have been formed into thin sheets have not been effectively detectable with prior technologies.

Similarly, in the fight against the illegal drug trade, there is a great need for a system that can quickly and accurately detect drugs inside sealed containers, mail parcels, and other small packages. Conventional drug detection methods are time-consuming, costly, and have had only marginal reliability.

NQR is a branch of radio frequency spectroscopy that has been used for the detection of explosives and drugs. NQR exploits the inherent electrical properties of atomic nuclei. Nuclei with non-spherical electric charge distributions possess electric quadrupole moments. In solid materials, electrons and atomic nuclei produce electric field gradients. These electric field gradients interact with the nuclear quadrupole moments of quadrupolar nuclei, producing energy levels for the quadrupolar nuclei, and hence their characteristic transition frequencies. Measurements of these frequencies, or relaxation time constants, or both, can indicate not only which nuclei are present but also their chemical environment.

The phenomenon of NQR is possible because, when a quadrupolar atomic nucleus is within an electric field gradient, the quadrupoles experience a torque, which causes the nucleus to precess about the electric field gradient. This precessional motion causes the nuclear magnetic moment to also precess. An externally applied radio frequency (RF) magnetic field having a frequency at or near the quadrupole's precessional frequency results in resonance between the applied RF magnetic field and the nuclei's magnetic moment. This RF magnetic field, which is applied as a pulse, tips and momentarily synchronizes the orientations of the magnetic moments of these quadrupolar nuclei as they precess. As a result of this tipping of the orientations of the nuclei, which can also be described as the excitation of the nuclei to higher energy levels, the energy level within each nucleus is briefly not in equilibrium. After application of the external RF magnetic field has ceased, the magnetic moments of the nuclei move out of synchronization with each other as the nuclei begin to return to equilibrium. As the nuclei move out of synchronization, they cumulatively generate an RF signal known as the free induction decay (FID) signal. The transmission of additional appropriate RF pulses can cause the generation of additional FID signals, and can also cause the generation of additional signals known as echoes, also referred to as spin-echoes. The spin-echoes are generated as the orientations of the magnetic moments of the nuclei pass through a synchronized orientation. A pick-up coil is used to detect both the FID and echo signals generated by the nuclei, which are subsequently received and amplified by a sensitive receiver.

Any chemical element's nucleus that has a spin quantum number greater than one-half has a non-spherical charge distribution, and can therefore exhibit quadrupolar resonance. Many nuclei have been identified that exhibit quadrupolar resonance, including: ${}^7\text{Li}$, ${}^9\text{Be}$, ${}^{14}\text{N}$, ${}^{17}\text{O}$, ${}^{23}\text{Na}$, ${}^{27}\text{Al}$, ${}^{35}\text{Cl}$, ${}^{37}\text{Cl}$, ${}^{39}\text{K}$, ${}^{55}\text{Mn}$, ${}^{75}\text{As}$, ${}^{79}\text{Br}$, ${}^{81}\text{Br}$, ${}^{127}\text{I}$, ${}^{197}\text{Au}$, and ${}^{209}\text{Bi}$. A significant factor in contraband detection by means of NQR is that quadrupolar nuclei that are commonly present, and potentially readily observable, in explosives and drugs include nitrogen (${}^{14}\text{N}$), chlorine (${}^{35}\text{Cl}$, ${}^{37}\text{Cl}$), sodium (${}^{23}\text{Na}$), and potassium (${}^{39}\text{K}$). The hydrochloride forms of drugs, such as cocaine hydrochloride, contain the quadrupolar nuclei ${}^{35}\text{Cl}$ and ${}^{37}\text{Cl}$. ${}^{14}\text{N}$ is the most studied quadrupole nucleus for explosives and narcotics detection, because ${}^{14}\text{N}$ is a constituent element of both explosives and drugs, including 2,2-bis[(nitroxy)methyl]-1,3-propanediol dinitrate (commonly referred to as PETN), cocaine base, cocaine hydrochloride, and heroin based drugs.

The frequencies of the NQR signals generated by quadrupolar nuclei are an important distinguishing feature of the NQR signals. An NQR frequency of a nucleus is equal to the precessional frequency of the nucleus, which is determined both by the characteristics of the quadrupolar nucleus and by the local electronic environment of the nucleus. Importantly, due to differences between the local crystalline environments of different substances, the resonant frequencies of an element that may be present in many substances, ${}^{14}\text{N}$ for example, are different in each substance. The

resonant frequencies of an element may also be different in electronically inequivalent sites within a given substance. However, each resonant frequency is unique, well defined, and consistent.

In addition to the resonance frequencies, relaxation times of quadrupolar nuclei are other distinguishing features of an NQR response. Resonance frequencies and relaxation times are compound-, molecular site-, temperature-, and pressure-specific. The repetition rate and timing of RF pulses required for exciting and detecting a specific NQR signal are determined by relaxation times. Relaxation times can be as short as a few microseconds or as long as many seconds. The fundamental relaxation times are designated T_1 , the spin-lattice relaxation time; T_2^* , the FID decay time constant; T_2 , the spin-spin relaxation time; and $T_{2\text{-eff}}$ (T_2 effective), the echo train decay time constant. The spin-lattice relaxation time T_1 is indicative of the time required for the nuclear spin system to return to equilibrium with its surroundings following a disturbance such as a resonant RF pulse. The FID decay time constant T_2^* is the time constant of the decay of FID signals. The spin-spin relaxation time T_2 is the time constant of the decay of a two-pulse echo sequence. For spin-lock spin-echo (SLSE) pulse sequences (discussed below), the peak echo amplitudes decrease exponentially with a time constant $T_{2\text{-eff}}$.

The presence and identity of explosives or drugs in a container is determined with an NQR system by irradiating the container with RF signals at or near a known NQR frequency of a target substance, and then detecting any quadrupolar resonance signals created by the application of the RF signal. The quadrupolar resonance signals, if any, are received by a receiver, and the output of the receiver is digitized and inputted to a computer. The computer compares the received signals with known parameters of a target substance, thereby determining whether the target substance is present. The process is then repeated by transmitting RF signals at NQR frequencies of additional target substances. Previous work in this area is reflected in U.S. patent 5,592,083 to Magnuson *et al.*, ("Magnuson '083") for a "System and Method for Contraband Detection Using Nuclear Quadrupole Resonance including a Sheet Coil and RF Shielding Via Waveguide Below Cutoff."

It is widely known in the NQR art that the RF signals transmitted by NQR detection systems can induce undesirable magneto-acoustic ringing in magnetized materials, for example iron, ceramics, coating materials, spring steel, and even paper clips. It is generally believed that magneto-acoustic ringing is the result of ferromagnetic domains in magnetized materials attempting to realign in response to the applied RF magnetic field. This vibration of the ferromagnetic domains causes lattice distortions that reflect back and forth within the material, resulting in the transmission of RF waves near the frequency of, and in phase with, the applied RF

magnetic field. This ringing may last on the order of a millisecond and may have an amplitude comparable to or much greater than the amplitudes of NQR signals transmitted from explosives or drugs. The RF signals transmitted by NQR systems can also excite undesirable piezo-electric ringing signals, which are interfering signals similar to magneto-acoustic ringing signals. Electronic circuit ringdown, and baseline offset are other undesirable signal artifacts that commonly exist in NQR systems.

The reliability of NQR systems for the detection of explosives and drugs can be significantly reduced due to magneto-acoustic ringing, piezo-electric ringing, electronic circuit ringdown, and baseline offset. The reliability is reduced because magneto-acoustic ringing signals and piezo-electric signals appear to be NQR signals from a target substance, which results in the system mistakenly indicating the presence of a target substance. Occurrences of this type of mistaken identification can be reduced by increasing the threshold level at which received signals are interpreted as NQR signals from a target substance. However, increasing the threshold level reduces the sensitivity of the system, which undesirably increases the size of the minimum detectable quantity of a target substance. Electronic circuit ringdown and baseline offset introduce signal errors that also can result in mistaken identification or non-identification of target substances.

U.S. patent 5,365,171 to Buess *et al.* ("Buess '171") for "Removing the Effects of Acoustic Ringing and Reducing Temperature Effects in the Detection of Explosives by NQR" discloses a system and method for removing the effects of magneto-acoustic ringing in some NQR applications. Buess '171 discloses a system in which a specimen is irradiated with a modified steady state free precession (SSFP) pulse sequence that is a combination of two SSFP pulse sequences, a phase-alternated pulse sequence (PAPS) and a non-phase-alternated pulse sequence (NPAPS). In SSFP pulse sequences, including the PAPS and NPAPS pulse sequences disclosed in Buess '171, each pulse functions as an excitation pulse. As specified in Buess '171, portions of the PAPS and NPAPS NQR response signals are added together or subtracted from each other, which results in removal of the FID contribution and also cancels out the magneto-acoustic ringing. However, as elaborated below, the system and method for removing magneto-acoustic ringing disclosed in Buess '171 are not useful for the detection of substances in which the ratio of T_1/T_2 for the quadrupolar nuclei of interest is greater than about five, and they are not useful in most applications for the detection of substances in which the quadrupolar nuclei of interest have a T_1 value that is greater than about one second.

When irradiated with SSFP pulse sequences, substances in which the quadrupolar nuclei of interest have a ratio of T_1/T_2 that is greater than about five produce very small amplitude NQR responses. These small amplitude NQR responses

are not large enough to be useful for the detection of explosives or drugs. Consequently, SSFP pulse sequences, which include the PAPS and NPAPS pulse sequences used in the system and method disclosed in Buess '171, are not useful for the detection of quadrupolar nuclei in explosive or drug substances in which the ratio of T_1/T_2 is greater than about five. The nucleus of ^{14}N in PETN, a common ingredient in many plastic explosives, has a ratio of T_1/T_2 that is greater than five under conditions appropriate for detection.

In addition to SSFP pulse sequences, spin-locked spin-echo (SLSE) pulse sequences have been widely used in NQR systems. Early references to SLSE pulse sequences include R. A. Marino *et al.*, "Multiple Spin Echoes in Pure Quadrupole Resonance," Journal of Chemical Physics, Vol. 67, pp. 3388 *et seq.*, 1977, and R. A. Marino, "Detection and Identification of Explosives by ^{14}N in NQR," Proceedings of the New Concepts Symposium and Workshop on Detection and Identification of Explosives, pp. 399 *et seq.*, Reston, Virginia, October 1978. A SLSE pulse sequence consists of an excitation pulse followed by a number of refocusing pulses, with each refocusing pulse having the same phase, which is ninety degrees from the phase of the excitation pulse. SLSE pulse sequences are effective for producing NQR echo signals. However, using multiple SLSE pulse sequences to reduce magneto-acoustic ringing or piezo-electric ringing has not proven effective for NQR detection.

In order to achieve artifact rejection when using a SLSE pulse sequence, the SLSE pulse sequence is typically performed two or more times, and a waiting time is required between repetitions of the SLSE pulse sequence. The waiting time required is a minimum of about 0.5 times T_1 , and is ideally about three times T_1 . Thus, in NQR detection systems using SLSE pulse sequences, two or more pulse sequences, and three or more T_1 's may be required. To maintain the same level of sensitivity when the value of T_1 increases, the time required for detection must also increase. Consequently, for most applications, it is not time effective to use SLSE pulse sequences for the detection of substances in which T_1 is greater than about one second, and this is especially true for substances such as PETN in which T_1 is much greater than one second. Also, as stated above, SLSE pulse sequences have not proven practical for the elimination of magneto-acoustic ringing or piezo-electric ringing.

In addition to undesirable signal artifacts, temperature effects can also degrade the performance of NQR detection systems. Due to temperature effects, an actual NQR frequency of a quadrupolar nucleus may be offset from the expected value. This can result in the frequency of the transmitted RF pulses being too distant from the actual resonant frequency to produce resonance. In order for the excitation to produce resonance, the frequency of the transmitted RF waves must generally fall within a band of frequencies that is about two thousand Hz wide centered around the actual

NQR frequency of the quadrupolar nuclei to be detected. If the transmitted frequency is outside of this band of frequencies, no NQR echo signals will be generated by the quadrupolar nuclei and the NQR detection system will erroneously indicate the absence of a target substance that is actually present in the specimen.

Broadly speaking, this invention provides a practical method and system for improving the performance of a nuclear quadrupole resonance (NQR) system used for detecting substances, such as explosives and drugs, that may be present in a specimen. More particularly, the invention provides for the cancellation of extraneous signals in an NQR detection system.

The present invention entails irradiating the specimen with a specific sequence of electromagnetic pulses, referred to as a spin-locked inversion mid-echo (SLIME) pulse sequence. The SLIME pulse sequence has only one excitation pulse. Each pulse in the SLIME pulse sequence has a specified phase and duration, and the pulses are separated by specified time intervals. The frequency of the pulses is chosen to be at or near an NQR resonant frequency of specific quadrupolar nuclei in a target substance. If the target substance is present, the SLIME pulse sequence manipulates the orientations of the magnetic moments of these quadrupolar nuclei, causing these quadrupolar nuclei to generate oppositely-phased sets of NQR echo signals. The NQR echo signals, along with extraneous signals that may be present, such as magneto-acoustic ringing signals and piezo-electric ringing signals, are received by the NQR detection system. Other extraneous signals that are generated within the NQR detection system may also be present, such as electronic circuit ringing and baseline

offset. Unlike the oppositely-phased NQR echo signals, the extraneous signals detected by the NQR detection system such as magneto-acoustic ringing, piezo-electric ringing, electronic circuit ringing, and baseline offset are not oppositely-phased.

After the NQR echo signals are received, NQR echo signals of one phase are subtracted from NQR echo signals having the opposite phase, rendering a cumulative echo signal, and simultaneously subtracting out the same-phase extraneous signals. Because the SLIME pulse sequence is not a steady state free precession (SSFP) pulse sequence, the SLIME pulse sequence can be used to eliminate extraneous signals and to detect substances in which the nuclei of interest have a ratio of T_1/T_2 (spin-lattice relaxation time/spin-spin relaxation time) greater than five. The SLIME pulse sequence can also be used to eliminate extraneous signals and to detect substances in which the nuclei of interest have a spin-lattice relaxation time T_1 greater than one second, even in applications allowing only a limited amount of time for detection, because the SLIME pulse sequence has only a single excitation pulse.

The invention is described further hereinafter, by way of example only, with reference to the accompanying drawings, in which:

FIG. 1A (prior art) is a graph of a PAPS SSFP pulse sequence;

FIG. 1B (prior art) is a graph of a NPAPS SSFP pulse sequence;

FIG. 1C (prior art) is a graph of a SLSE pulse sequence, including a representative NQR echo signal;

FIG. 2A is a timing diagram of a first embodiment of the SLIME pulse sequence of the present invention, including representative NQR echo signals;

FIG. 2B is a representative cumulative NQR echo signal derived from the NQR echo signals shown in FIG. 2A;

Our ref: 23116-0:LJBG:sp
Your ref: Canadian Pat 2144540
Contact: Boris Golja
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Invention Technologies Pty Ltd
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Attention: Mr M M Bebich

Dear Matthew

Canadian Patent Application 2144540
Invention Technologies Pty Ltd
Fire Extinguishing Apparatus

Further to our previous correspondence on the above application, the most recent being our 8 November 2005 letter, as we did not receive your instructions by 15 November 2005, we understand that you are not interested in maintaining this application any longer and it will therefore become abandoned through failure to file a response to the examiner's Office Action by the extended date of 8 January 2006. We shall not send you any further reminders in relation to the response date and approaching abandonment of the application, and shall presently close our file.

Yours faithfully
WRAY & ASSOCIATES

Boris Golja

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